IMPROVEMENT OF THE QUALITY ASSURANCE IN TRITIUM ANALYSES IN WATERS BY LSC

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**INTRODUCTION**

**Tritium (³H)**

- Present in the environment as a result of both natural and anthropogenic sources

<table>
<thead>
<tr>
<th>³H</th>
<th>Half-life</th>
<th>Pure beta emitter</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>12.32 years</td>
<td>$E_{\text{max}} = 18.6\text{KeV}$</td>
</tr>
</tbody>
</table>

- Produced in the atmosphere through nuclear reactions between fast neutrons resulting from cosmic radiation and nitrogen atoms

- Nuclear tests (1945-1963) → Contamination by Fallout

- Nowadays → Levels near the minimum detectable concentrations
Nuclear and Technological Institute (ITN)
- Radiological Protection and Safety Unit (UPSR)
- Environmental Radioactivity Group

Requested by water suppliers to carry out tritium analyses in drinking waters
INTRODUCTION

Nuclear and Technological Institute (ITN)

Improvement of the method

- Portuguese Standard Guideline NP 4362/1997
  - Until the middle of 2009
    - Internal standard for each sample
    - Samples controlled by volume
    - DL = 8.0 Bq L\(^{-1}\), 150min

- Internal Method
  - ISO standard CD 9698/2008
    - Control of the quenching interference through a calibration curve
    - Sample volume started to be controlled by weighing
    - DL = 4.0 Bq L\(^{-1}\), 120min
INTRODUCTION

Nuclear and Technological Institute (ITN)

Improvement of the method

Quality Assurance Program

- Validation of analytical method;
- Resources used for the laboratory analysis procedures for sample handling and analysis;
- Quality control;
- Monitoring and auditing.
Nuclear and Technological Institute (ITN)

Improvement of the method

Quality Assurance Program

Validation of analytical methodology:

Studies ensuring that the method is fit-for-purpose:

- Analytical thresholds;
- Accuracy (trueness and precision);
- Curve fitting and its range;
- Budget uncertainties.
INTRODUCTION

Nuclear and Technological Institute (ITN)

Improvement of the method

Quality Assurance Program

✓ Validation of analytical methodology

Submitted for accreditation to the Portuguese accreditation body (IPAC) in October of 2009.
**EXPERIMENTAL PROCEDURE**

**3H Determination**

- The radioactive sample is combined with a liquid scintillation cocktail and the radionuclide decay produces an ionizing particle;
- Part of the kinetic energy of this ionizing particle is transferred to the scintillator and converted into light during the radioactive decay process;
- Purification by distillation;
- Addition of 0.5g of Na$_2$S$_2$O$_3$ and 1g of Na$_2$CO$_3$ to a volume of about 250 mL;
- An aliquot of the distillate (about 8 g) is mixed with 12g of Ultima Gold LLT scintillation cocktail in borosilicate glass vials.
**EXPERIMENTAL PROCEDURE**

**3H Determination**

- Samples are stabilized in the dark;
- Tri-Carb 3170 TR/SL (Packard), in low level mode;
- DL $\approx 4.0$ Bq L$^{-1}$, 120min (routine analysis).
**EXPRESSIONS**

### Activity Calculation

\[ c_A = \frac{n}{\varepsilon \cdot V} \quad \text{Net count rate} \]

\[ V = \frac{m}{\rho_{H_2O}} \]

### Expanded uncertainty

\[ u(c_A) = c_A \sqrt{u^2_r(n) + u^2_r(\varepsilon) + u^2_r(V)} \]

### Characteristic limits

**Decision threshold**

\[ c_A^* = \frac{k}{\varepsilon \cdot V} \sqrt{\frac{b}{t} + u^2(b)} \]

**Detection limit**

\[ c_A^# = \frac{2 \cdot c_A^* + \frac{k^2}{t \cdot \varepsilon \cdot V}}{1 - k^2 \cdot (\varepsilon \cdot V)^2 \left(u^2_r \cdot \varepsilon + u^2_r \cdot V\right)} \]

- \( c_A \): Activity, Bq L\(^{-1}\)
- \( n \): Net count rate
- \( \varepsilon \): Efficiency
- \( V \): Sample volume, L
- \( m \): Sample mass, kg
- \( \rho_{H_2O} \): Water density, kg L\(^{-1}\)
- \( k \): Expansion Factor
- \( t \): Counting time, s
- \( b \): Background count rate
STEPS FOR QUALITY IMPROVEMENT

- Equipment Calibration
- Method Validation
- Quality Control
STEPS FOR QUALITY IMPROVEMENT

Equipment Calibration

- 10 standard samples ≈ 175 Bq each
- CCl₄ (µL): 2, 4, 6, 8, 10, 12, 14, 16, 18, 20
- Calibration curve

\[ \varepsilon = (1.18 \pm 0.43) \times 10^{-1} + (3.43 \pm 0.13) \times 10^{-3} \cdot tSIE \]
STEPS FOR QUALITY IMPROVEMENT

- Equipment Calibration
- Method Validation
  - Detection Limit

Detection Limit = 1.6 Bq L\(^{-1}\)

Routine measurements

24h counting time
STEPS FOR QUALITY IMPROVEMENT

Equipment Calibration

Method Validation

✓ Detection Limit

✓ Accuracy (Trueness and Precision)

Trueness

- Two intercomparison exercises

<table>
<thead>
<tr>
<th>Year</th>
<th>Z-score</th>
</tr>
</thead>
<tbody>
<tr>
<td>2004</td>
<td>2.14</td>
</tr>
<tr>
<td>2008</td>
<td>2.35</td>
</tr>
</tbody>
</table>

2 < |Z| ≤ 3  →  Acceptable

Precision

- Precision acceptance criterion of 10.0%

- 10 sub-samples of a control sample: $\approx 50$ Bq L$^{-1}$

2.4% → Acceptable
STEPS FOR QUALITY IMPROVEMENT

Equipment Calibration

Method Validation

- Detection Limit
- Accuracy (Trueness and Precision)
- Budget Uncertainties

Net count rate

\[ u(c_A) = c_A \sqrt{u_r^2(n) + u_r^2(\epsilon) + u_r^2(V)} \]

\[ u(n) = \sqrt{u^2(g) + u^2(b)} \]

\[ u(g) = \frac{g}{\sqrt{t}} \]

\[ u(b_k) = \frac{b_k}{\sqrt{t_k}} \]
STEPS FOR QUALITY IMPROVEMENT

- Equipment Calibration
- Method Validation
  - Detection Limit
  - Accuracy (Trueness and Precision)
  - Budget Uncertainties

\[ u(c_A) = c_A \cdot \sqrt{u_r^2(n) + u_r^2(\varepsilon)} + u_r^2(V) \]

Efficiency

\[ \varepsilon = a_0 + a_1 \cdot tSIE \] (Least squares method)

\[ u(\varepsilon) = \sqrt{u^2(a_0) + tSIE^2 \cdot u^2(a_1) + a_1^2 \cdot u^2(tSIE)} \]
STEPS FOR QUALITY IMPROVEMENT

- **Equipment Calibration**
- **Method Validation**
  - ✓ Detection Limit
  - ✓ Accuracy (Trueness and Precision)
  - ✓ Budget Uncertainties

![Mathematical equation]

\[
u(c_A) = c_A \sqrt{u_r^2(n) + u_r^2(\varepsilon)} + u_r^2(V)
\]

**Equivalent volume**

\[
V = \frac{m}{\rho_{H_2O}}
\]

\[
u(V) = V \sqrt{u_r^2(m) + u_r^2(\rho_{H_2O})}
\]

\[
u(m_X) = \sqrt{2}.u(m_T)
\]

\[
\rho_{H_2O} = 1.0 \pm 0.0 \text{ g. cm}^{-3}
\]
STEPS FOR QUALITY IMPROVEMENT

- Equipment Calibration
- Method Validation
  - Detection Limit
  - Accuracy (Trueness and Precision)
  - Budget Uncertainties

\[ u(c_A) = c_A \cdot \sqrt{u_r^2(n) + u_r^2(\varepsilon) + u_r^2(V)} \]

Efficiency: 24%
Net Count Rate: 76%
Equipment Calibration
Method Validation
Quality Control
- **Internal QC**
  - Implementation of ISO/IEC 17025;
  - Storage improvements (tightness of the sample containers and temperature);
  - Samples and standards prepared by weighing;
  - Equipment performance tests.
STEPS FOR QUALITY IMPROVEMENT

- Equipment Calibration
- Method Validation
- Quality Control
  - ✔ Internal QC (Control Charts)

Warning Limits: $\overline{X} \pm 2\sigma$
Action Limits: $\overline{X} \pm 3\sigma$

Trueness of the method
STEPS FOR QUALITY IMPROVEMENT

- Equipment Calibration
- Method Validation
- Quality Control
  - Internal QC (Control Charts)

Warning Limits: $\bar{X} \pm 2\sigma$
Action Limits: $\bar{X} \pm 3\sigma$

Blank Samples
STEPS FOR QUALITY IMPROVEMENT

- Equipment Calibration
- Method Validation
- Quality Control
  - Internal QC
  - External QC
  - Proficiency tests

| Year | |z-score| |
|------|------------------|
| 2009 | 0.03 |

\[|Z| \leq 2 \text{ satisfactory}\]

- Revalidate the method and to check the performance of the technicians
The change introduced in the method allowed to improve the results and consequently analytical data with better quality are available to the customers.

The requirements for a quality system according to EN ISO/IEC 17025 must be fulfilled in order to get the accreditation of the analytical techniques.

To keep the analytical process up to date, it is essential to participate in intercomparison exercises and to maintain internal and external audits.
Thank you for your time!
Any questions?